MINERALOGICAL CHARACTERIZATION OF FE-BEARING AGB AND SUPERNOVA SILICATE GRAINS FROM THE QUEEN ALEXANDRA RANGE 99177 METEORITE.

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Introduction: Spectroscopic observations of the circumstellar envelopes of evolved O-rich stars indicate the dust is mostly amorphous silicate with olivine-like compositions [1]. Spectral modeling suggests these grains are Fe-rich [Mg/(Mg+Fe) ~0.5] [2], but it is not known whether the Fe is distributed within the silicate matrix or exists as metal inclusions [3, 4]. In contrast, the crystalline silicates are inferred to be extremely Mg-rich [Mg/(Mg+Fe) > 0.95] [5]. The mineralogies and chemical compositions of dust in supernova (SN) remnants are not as well constrained, but abundant silicates of olivine-like and enstatite-like compositions have been fit to the infrared emission features [6]. Silicates in the interstellar medium (ISM) are >99% amorphous and Fe-bearing [7]. The dearth of crystalline silicates in the ISM requires that some amorphization or destruction mechanisms process these grains [8].

Mineral and chemical studies of presolar grains by transmission electron microscopy (TEM) reveal incredible details that cannot be discerned by traditional astronomy, including compound grains, inclusions, chemical heterogeneities, and evidence for ISM processing [9]. The mineral and chemical characteristics of presolar silicates are particularly diverse. Most of the ~50 presolar silicates studied by TEM are amorphous and Fe-bearing ([10] and refs. therein), consistent with astronomical observations. However, some of the grains have evidence for incorporation of Fe during parent body alteration.

In this study, we report the isotopic and mineralogical examination of three presolar silicates from QUE 99177 (CR3), an unequilibrated meteorite with a high abundance of presolar silicates that have likely escaped extensive alteration on the parent body [11-13].

Methods: A separate of fine-grained matrix material from QUE 99177 was prepared by repeated freeze-thaw and ultrasonication in milli-Q water. Soluble organic matter was removed and grains were separated by size by centrifugation in an isopropanol and water solution. Grains smaller than ~2 μm were deposited onto Au foil. Dense grain regions were analyzed for their O and Si isotopes by raster ion imaging with the JSC NanoSIMS 50L. A Cs^+ primary ion beam of ~1.4 pA for session #1 and ~3.9 pA for session #3 was rastered over 20 μm fields of view for multiple planes. The O and Si isotopes were measured simultaneously as negative secondary ions.

Three relatively large (> ~300 nm) grains with anomalous O isotopic compositions were selected for mineralogical characterization. Electron transparent cross-sections of the grains were produced by focused ion beam (FIB) milling. Grains 1_15_1a and 1_15_1b were only 4 μm apart and were extracted in one section. Carbon caps were first deposited on the grains of interest followed by electron beam deposited Pt. The entire sections were then covered with ion beam deposited Pt straps, lifted out, and thinned to <100 nm. The C caps served as markers to ensure the correct grains were sectioned. The grains were imaged and analyzed for their microstructures and chemical compositions with the JSC JEOL 2500 field-emission scanning TEM. Elemental maps were acquired with a Noran thin window EDX spectrometer using a 2 nm incident probe. Electron diffraction and dark-field (DF) imaging were used to determine grain crystallinity.

Results: Grains 1_15_1a and 3_10_13 are both enriched in ^{17}O ($\delta^{17}O = 1190 \pm 140$ ‰ and 2230 ± 250‰, respectively) and have normal Si isotopic compositions. These isotopic signatures indicate origins in low-mass asymptotic giant branch (AGB) stars. Grain 1_15_1a is ~540 × 240 nm in size in cross-section (Fig. 1). TEM analysis indicates the grain is amorphous with a nonstoichiometric chemical composition. The grain is very Mg-poor and Fe-rich [Mg/(Mg+Fe) (at.) = 0.04] and contains minor Al, Ca, and Ni. The pitted surface may have resulted from ion beam sputtering during the NanoSIMS analysis.

Grain 3_10_13 is ~500 × 325 nm in cross-section (Fig. 2). This grain is composed of Fe-rich amorphous silicates, or a mixture of nanocrystalline Fe-oxides and amorphous silicates, along with inclusions of crystalline silicates. The bulk grain has Mg/(Mg+Fe) = 0.26 and trace amounts of Al, Ca, and Ni. Several regions within the grain have higher Mg contents. The Mg-rich region on the left in Fig. 1C is an ~100 nm triangular crystalline pyroxene grain. To the right of this pyroxene is a small ~90 nm crystalline olivine (Fo70) grain.

Unlike the previous two grains, 1_15_1b is enriched in ^{18}O ($\delta^{18}O = 630 \pm 80$‰) and has normal $^{17}O/^{16}O$ and Si isotope ratios. This grain most likely originated from a SN. TEM analysis of this grain indicates it is very similar to 1_15_1a. The grain is ~475 × 260 nm in cross-section (Fig. 3). It is amorphous and

has a nonstoichiometric Mg-poor and Fe-rich composition [Mg/(Mg+Fe) = 0.02] with minor Al, Ca, and Ni.
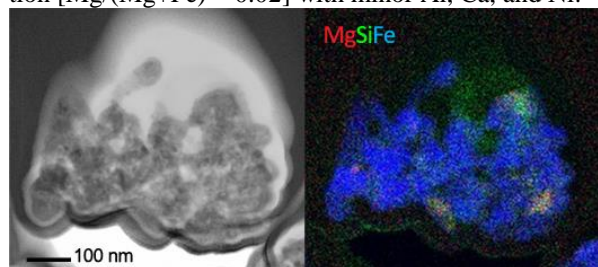

Figure 1. Bright-field (BF) STEM image of grain 1_15_1a and corresponding composite elemental map.
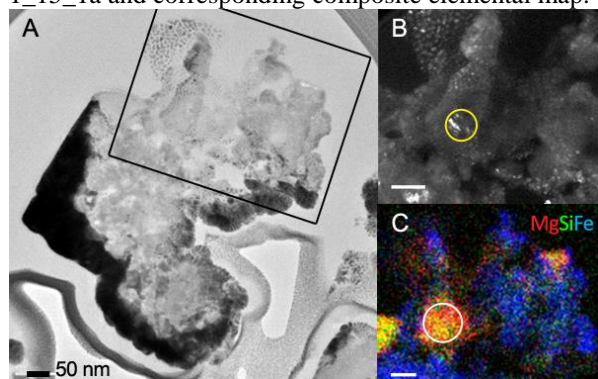

Figure 2. (A) BF STEM image of 3_10_13. (B) DF TEM image of part of grain containing crystalline olivine (circled). (C) Composite elemental map of region outlined in (A) with olivine grain circled.
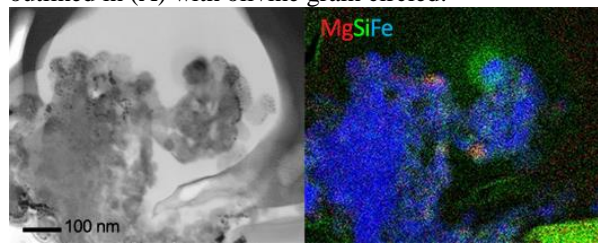

Figure 3. Bright-field (BF) STEM image of grain 1_15_1b and corresponding composite elemental map.

Discussion: Though they derive from very different stellar sources, grains 1_15_1a and 1_15_1b are very similar in terms of their structure and chemical composition. Overall, TEM analyses have not revealed systematic differences in the mineralogies of AGB and SN grains. For both types of sources, ~70% of the silicate grains are amorphous with varying chemical compositions and Fe contents. Chondritic porous interplanetary dust particles are more pristine than meteorites and the presolar silicates found in them include forsterite, equilibrated aggregates, and Mg-rich glass with embedded metal and sulfides (GEMS) having ~1.4–24 atom% Fe ([14] and refs. therein). Auger spectroscopic analyses of presolar silicates from QUE 99177 indicate Fe contents ~4.5–24 atom% [11], similar to presolar GEMS. Some presolar silicates from Acfer 094 and the altered meteorite Adelaide have up to ~45 atom% Fe [15-17]. The high Fe contents of the grains in Adelaide were attributed to thermal alteration [17]. The Fe abundances of the grains in this study (~21–34 atom% Fe) are slightly elevated from the Auger results for QUE 99177 and fall in the range observed for Acfer 094 and Adelaide.

We previously analyzed two presolar silicate grains from QUE 99177 [10]. One grain was a crystalline olivine and the other was an amorphous enstatite-like silicate with a nanocrystalline enstatite core and Fe in the perimeter. The latter grain was likely irradiated in the ISM and mildly altered on the parent body. The Fe in the grains in the current study, however, is much more abundant and is distributed uniformly rather than occurring as rims. If the Fe was acquired on the parent body, it could have been incorporated from neighboring Fe-rich grains that were thermally altered, similar to the scenario described by [17]. However, the amorphous matrix silicates in QUE 99177 are much less Fe-rich [13], so this alteration would have been localized. Irradiation of the grains in the ISM or by SN shocks could have sputtered Mg [18]. Alternatively, Fe could have been incorporated into the silicate lattice during condensation under non-equilibrium conditions at lower temperatures or in particularly Fe-rich gas [19].

Silicate 3_10_13 is more Mg-rich and Fe-poor than the other two grains. The crystalline silicate inclusions likely condensed at high temperatures ~1200–1300 K [20] and were incorporated into the amorphous silicate that formed at cooler temperatures ~800–950 K [21]. The preservation of small Mg-rich crystalline silicates makes it unlikely that this grain experienced extensive secondary alteration. In this case, it seems more plausible that the Fe was incorporated during condensation.

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